HIGH-RESOLUTION SOLID-STATE NMR OF MILK PRODUCTS

Solid-state ^{13}C and ^{31}P NMR spectroscopy was used to characterize individual milk components and freeze dried dairy products. Chemical shift correlations with secondary structure gave estimates of percent α-helix and β-sheet structures for native caseins not available from crystallography. Gaussian/Lorentzian lineshape analyses were used to observe the local conformational and motional characteristics of the materials. Phosphophorylated serine residues have a high degree of motional freedom, while the protein backbones appear to be fairly rigid. Lactose in the powdered dairy products studied is in a rigid crystalline environment as reflected in NMR lineshapes. Rotating frame relaxation measurements were used to characterize cation binding in metallated caseins. The effect of paramagnetic cations on proton $T_{1\rho}$ indicate that binding to serine phosphates is favored over binding to carboxylate residues. The analytical methodology used to characterize milk fractions was successfully applied to observing bulk structural and chemical changes during the production of dried milk products and cheeses. ^{13}C and ^{31}P CP/MAS spectra were sensitive to structural changes such as protein denaturation and aggregation as a function of such industrial processes as heat treatment in the production of milk powders and aging and pressing procedures in the production of cheeses. An application of the technique to the possible detection of adulteration in commercially produced dairy solids is also presented. J Magn Reson Anal 1996; 2:267-274.

Many nutritionally and commercially important dairy foods are solids, including milk powders, whey powders, coffee whiteners and cheeses. Solid-state NMR has proven to be a useful, non-destructive technique for obtaining detailed chemical information on the solid fat, protein and carbohydrate components of milk products. Single-pulse excitation, Magic Angle Spinning (MAS) techniques have been used to observe the ^{13}C signals of milk fat in cheese (1), while Cross Polarization (CP)/MAS techniques have been used to observe the ^{13}C signals of cheese proteins (1), crystalline lactose (2) and lactose-derived lactulose (3).

Much of the emphasis in milk protein chemistry has been in the study of casein micelles. These hydrated colloidal aggregates are responsible for the transport and delivery of protein, calcium and phosphate in milk products (4). Electron microscopic evidence showed an average colloidal particle size of 20-600 nm (5). Bovine milk contains predominantly four types of micellar casein: α_{S1}-,α_{S2}-, β- and κ-caseins (6), with κ-casein responsible for a diffuse, hydrophilic layer at the surface of the micelles commonly referred to as the "hairy" layer (7, 8). Small-angle X-ray (9) (SAXS) and neutron (10) scattering (SANS) studies support the presence of submicellar structure, with an average submicellar radius of 8.5-9 nm. The overall structure of the micelle has been described as a hydrated protein gel with individual casein submicelles cross-linked by microgranules of calcium phosphate (4) The structural and dynamic properties